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1 Your reference

SYN 51082

2 Patent application number
(The Patent Office will fill in this part)

0226178.2

11 NOV 2002

3 Full name, address and postcode of the or of each applicant (underline all surnames)

JOHNSON MATTHEY PLC
2-4 Cockspur Street
Trafalgar Square
London SW1Y 5BQ

Patents ADP Number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

64126303002

4 Title of the invention

Desulphurisation

5 Name of Your Agent (if you have one)

GIBSON, Sara Hillary Margaret

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Synetix Intellectual Property Department
PO Box 1, Room N205
Belasis Avenue
Billingham
Cleveland
England, TS23 1LB

Patents ADP Number (if you know it)

7912454002

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Country	Priority Application number (if you know it)	Date of Filing (day / month / year)
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7 If this application is divided or otherwise derived from an earlier UK application, give the number and filing date of the earlier application

Number of earlier application	Date of Filing (day / month / year)
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8 Is a statement of inventorship and of right to grant of a patent required in support of this request?

Yes

Answer yes if:

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Continuation sheets of this form -

Description 6

Claim(s) 1

Abstract 1

Drawings 1 + 1 + 1 *SW*

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Priority documents

Translations of priority documents

Statement of Invention and right to grant of a patent (*Patents Form 7/77*)

Request for Preliminary Examination and search (*Patents Form 9/77*)

Request for Substantive Examination (*Patents Form 10/77*)

Any other documents
(*Please specify*)

- 11 I/We request the grant of a patent on the basis of this application

Signature



Date

8.11.2002

- 12 Name and daytime telephone number of person to contact in the United Kingdom

SARA HILLARY MARGARET GIBSON
01642 522650

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Desulphurisation

This invention relates to desulphurisation and in particular to the desulphurisation of hydrocarbon streams.

Natural gas contains a variety of hydrocarbons, predominantly saturated, together with contaminants particularly sulphur compounds. It is often desirable to separate the hydrocarbon stream into fractions. The C_2 and higher hydrocarbons are generally separated from methane by liquefaction and then the resultant liquid stream, hereinafter natural gas liquids, may be separated into fractions, e.g. ethane, propane, butanes, and a higher hydrocarbon stream, hereinafter termed a gasoline fraction. In some instances it is desired to separate the butanes stream into n-butane and iso-butane.

The separation into fractions is usually effected by fractional distillation wherein the hydrocarbon feed is fed to a fractional distillation column. A temperature gradient is established between the top and bottom of the column so that the more volatile components are separated as an overhead gas stream while the less volatile components are discharged from the bottom of the column as a liquid stream. The column is usually operated with heat supplied to the lower end of the column by boiling part of the separated liquid stream and returning the vaporised liquid to the column. Similarly the vapour stream from the upper end of the column is cooled to condense part thereof. The condensate is returned to the upper end of the column.

The separation of the natural gas liquids is often effected in a series of stages. In a first stage, the ethane is separated as the overhead stream in a first column, termed a de-ethaniser, giving a liquid stream containing C_3 and higher hydrocarbons. This stage is normally effected at elevated pressure with refrigeration to condense the liquid phase. The liquid stream containing C_3 and higher hydrocarbons is then fed to a second column, termed a de-propaniser, wherein the propane is separated as the overhead gaseous phase. The resulting C_3 -depleted liquid hydrocarbon stream is then fed to a further column, termed a de-butaniser, wherein butanes are separated as the overhead stream from higher hydrocarbons. The higher hydrocarbons form the gasoline fraction. As indicated above in some cases the butanes stream may be separated into normal and isobutane by means of a butanes splitter column. So that water can be used to effect the cooling of the overhead stream in the de-propaniser and de-butaniser (and butanes splitter, if used), the distillation is effected at such an elevated pressure that the temperature of the vapour fed to the overhead condenser is at a temperature in the range 50 to 100°C.

Natural gas generally contains a variety of sulphur compounds including hydrogen sulphide, carbonyl sulphide, alkyl mercaptans, alkyl sulphides and disulphides. The atmospheric pressure boiling points of the common sulphur contaminants and the paraffins is shown in the following table.

Catalysts that may be used to effect the oxidation include the catalysts, which are generally copper-based, that have been used in the aforementioned hydrocarbon sweetening process.

5 A typical catalyst is a granular material sold by Syntex as Syntex KSR and comprises 10-12% by weight copper sulphate, 6-8% by weight sodium chloride and 10-20% by weight of water on a clay support. This is active at the temperatures prevailing in the distillation column. In order to maximise the activity of the catalyst it may be necessary to adjust the water content of the feed to maintain the water content of the catalyst at or near its optimum value by balancing the water added, and the water produced by the reaction, with the water removed in
10 the overhead and liquid fractions. Generally, the amount of water that need be incorporated into the hydrocarbon feed is such that it is miscible with the hydrocarbon stream under the prevailing conditions.

The catalyst is preferably disposed as a fixed bed within the distillation column. A column having a modular packing structure may be employed with the catalyst loaded as an
15 individual bed in each module.

The invention is illustrated by reference to the accompanying drawing which is a diagrammatic flowsheet of one embodiment of the invention.

In the drawing there is shown a de-butaniser fractional distillation column 10 used for the separation of butanes from the liquid hydrocarbon stream from a de-propaniser. The liquid
20 hydrocarbon stream 12 is supplied to the column at a location part way up the column. Typically the column may have 20 or more stages and typically at least a third, preferably at least half, but not more than three quarters, of the stages will be below the location at which the feed is supplied. The column is provided at its lower end with a liquid offtake 14. Part of the liquid hydrocarbon stream removed from the bottom of the column is heated in a reboiler 16
25 and recycled to the lower end of the column via line 18. The remainder of the liquid stream from the lower end of the column constitutes a gasoline stream.

At the upper end of the column 10 an overhead vapour stream, comprising the butanes, is taken via line 20. This vapour is cooled in a heat exchanger 22, which may be cooled by water or air, to condense the vapour which is fed to a drum 24. Part of the condensed liquid
30 butanes are recycled to the top of the column via line 26 and the remainder taken as a product butanes stream 28. Disposed in the column, preferably above the hydrocarbon feed location, is a fixed bed 30 of an oxidation catalyst, for example Syntex KSR. Lines 32 and 34 are provided for the injection of air and water respectively into the hydrocarbon feed stream 12.

35 The column is operated at such a pressure, e.g. 10 bar abs., that the temperature of the vapour in line 20 is in the range 50 to 100°C. Typically the temperature of the liquid stream at the lower end of the column is 20 to 60°C greater than that of the vapour in line 20.

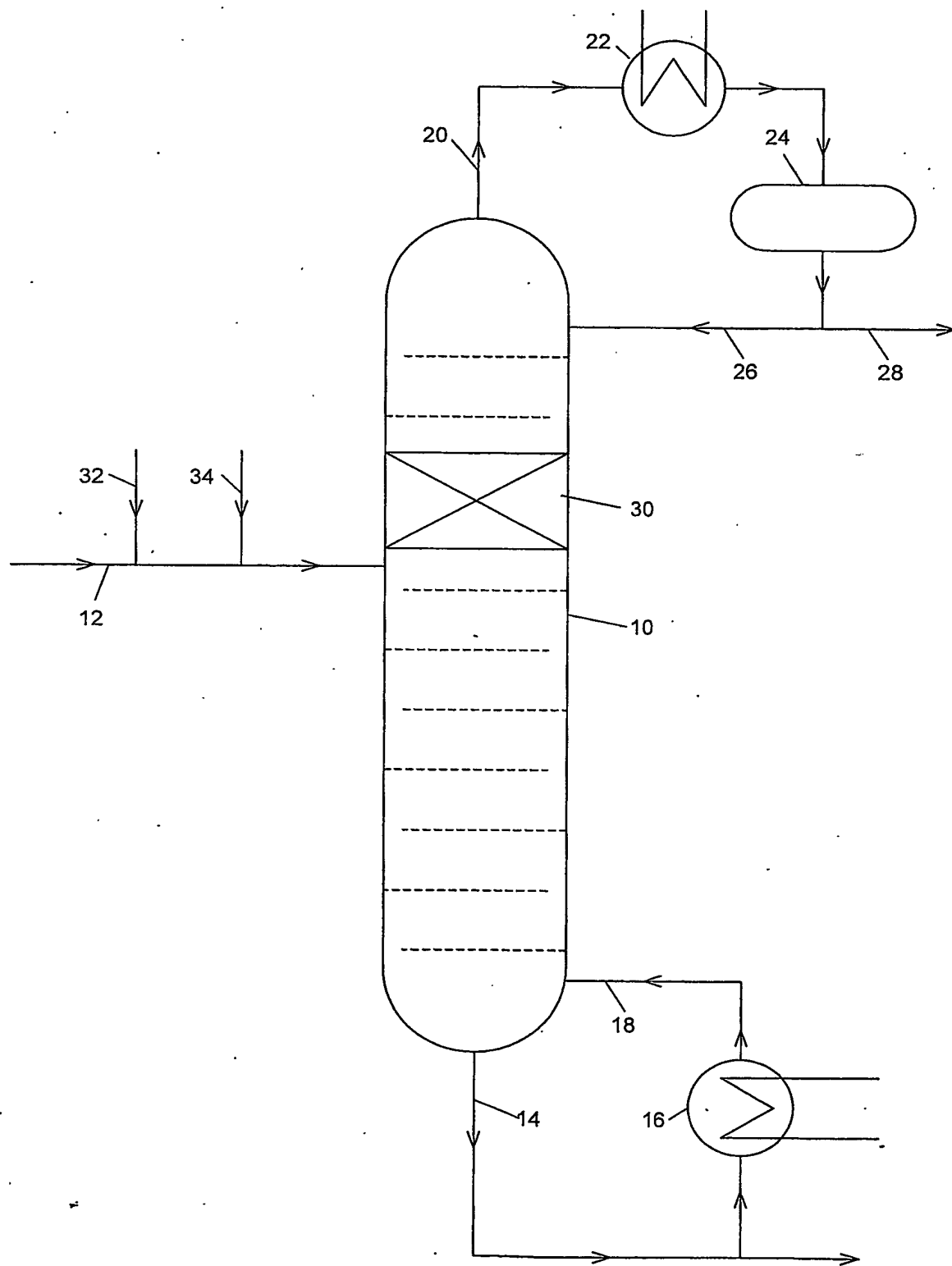
In operation a small amount of air and water are injected into the hydrocarbon feed stream 12. The amounts of air and water injected are such that they dissolve in the

Claims

1. A process for the separation of a stream containing propane and/or butanes from a hydrocarbon feedstock contaminated with alkyl mercaptans by fractional distillation at such a pressure that the separated overheads stream containing said propane and/or butanes is at a temperature in the range 50 to 100°C, comprising introducing sufficient oxygen into said hydrocarbon feedstock to oxidise the mercaptans therein and subjecting the resultant mixture to the fractional distillation in a column including at least one bed of a catalyst capable, under the prevailing conditions, of oxidising mercaptans to higher boiling point sulphur compounds, and separating the higher boiling point sulphur compounds as part of the liquid phase from the distillation.
2. A process according to claim 1 wherein the catalyst comprises a granular material containing copper sulphate, sodium chloride and water on a clay support.
3. A process according to claim 1 or claim 2 wherein the amount of mercaptans present in the hydrocarbon feedstock is less than 2000 ppm by volume.
4. A process according to any one of claims 1 to 3 wherein the distillation is effected at a pressure in the range 5 to 25 bar abs.
5. A process according to any one of claims 1 to 4 wherein the oxygen is supplied by dissolving air in the hydrocarbon feedstock.
6. A process according to any one of claims 1 to 5 wherein water is incorporated into the hydrocarbon feed in such an amount that it is miscible with the hydrocarbon stream under the prevailing conditions.

Abstract

Propane and/or butanes are separated from a hydrocarbon feedstock contaminated with alkyl mercaptans by fractional distillation at such a pressure that the separated overheads stream containing said propane and/or butanes is at a temperature in the range 50 to 100°C. Sufficient oxygen is introduced into the hydrocarbon feedstock to oxidise the mercaptans therein and the resultant mixture is subjected to the fractional distillation in a column including at least one bed of a catalyst capable, under the prevailing conditions, of oxidising the mercaptans to higher boiling point sulphur compounds. These higher boiling point sulphur compounds are separated as part of the liquid phase from the distillation.



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